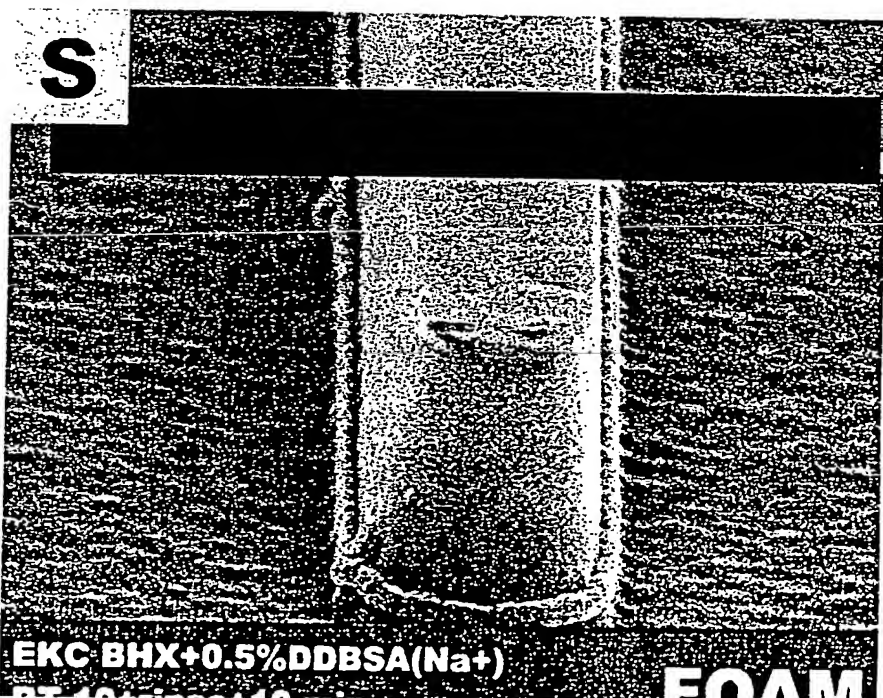


EXHIBIT A

S



EKC-BHX+0.5%DDBSA(Na+)

FOAM

S

Photoresist Residue Removal Using Aqueous Foam

Proof of Concept Experiments

Paul A. Kittle, PhD
Aquafoam, Inc.

Robert Small, PhD
Mihaela Cernat, Bob Patel, Becky Hon
EKC Technology, Inc.

Introduction

Aqueous foam is generally recognized as the medium of choice for cleaning tasks ranging from domestic and household jobs, to large industrial applications (1,2). This fact has not been lost on the semiconductor manufacturing industry, as over the years there have been attempts to couple the advantages of aqueous foam cleaning to the special needs of wafer production (3,4). The most important experiment, indirectly defining that aqueous foam could be used for cleaning semiconductor wafers, was performed by Leenaars (5) who showed that a single laser generated bubble could be passed over the surface of a wafer producing nearly quantitative particle removal. A summary of aqueous foam cleaning as it pertains to semiconductor wafers reviews the theory and practice leading to the experiments described in this paper (6).

Objectives

- (1) Demonstrate that a liquid composition delivered to a semiconductor wafer substrate in a foam medium can provide cleaning results equivalent to the same composition delivered to the wafer in the liquid phase.
- (2) Demonstrate that only collapsing aqueous foam bubbles are capable of cleaning semiconductor wafer substrates, without the use of cleaning compositions, in a manner analogous to ultra- or megasonics cleaning.

Theory

The theory pertaining to the first objective involves the fundamentals of aqueous foams. When a suitable fluid is transformed into foam, energy is added during the process of mixing the expansion gas with the foamable liquid. When the foaming system is fully developed, for the mixing conditions utilized, the foam formation rate is equal to the foam decay rate – the system is in equilibrium. If this completely mixed equilibrium foam is discharged from the mixing system, the formation rate declines to zero, but the drainage rate remains the same. The important feature is the immediate onset of drainage - the instant the foam leaves the mixing system (7).

In simple foaming systems – water with low levels of surfactant – the foamable liquid with added expansion gas creates foam, and the draining process, in effect, releases the expansion gas, thereby regenerating the original foamable liquid. If the foaming system does not contain any high vapor pressure components, which could escape with the expansion gas, then the initial liquid and the post-drainage liquid will be the same composition.

Since the semiconductor wafer cleaning processes are generally restricted to the liquids covering the wafer surface, foam discharged onto a wafer surface will instantly generate a liquid surface covering with a composition equal to the original foamed liquid.

The conclusion is: if the original liquid can perform a cleaning operation in the condensed phase (liquid), then the corresponding liquid delivered to the substrate in a foam medium will perform the same cleaning operation.

The second objective supports the hypothesis that aqueous foam and megasonics are essentially equivalent with respect to transferring energy to the substrate surface. The theory and practice of megasonic cleaning have been extensively disclosed in the literature (8), so that topic will not be reviewed here.

The energy release from aqueous foam bubble bursting has been briefly summarized in modern literature (9), but the fundamentals start with Dupre (10) with some more recent special cases (11-13). Since rationalizing various theoretical interpretations is not an objective of this paper, a simple model can emphasize important characteristics.

The work expended to produce foam can be expressed:

$$Work = A\gamma = 4\pi r^2\gamma \text{ (ergs).}$$

Where A is the surface area of the bubbles and γ is the surface tension of the foamed solution. This is simplified by the assumption that the bubbles are spherical, which is sufficient for this analysis.

For simplicity, assume a monodisperse aqueous foam with a radius of 30μ , or 0.003 cm. , prepared from a foamable solution providing a surface tension of 50 dynes/cm (14). Each bursting bubble will discharge 0.0057 ergs .

Further, assume a 300 mm wafer, 707 sq. cm. exposed to a moving foam medium for 10 minutes with a 50% foam drain time equal to 10 minutes . Also, the assumed foam flow rate maintains the wafer surface bubble concentration. During this treatment period, the wafer surface will be exposed to $25,000,000$ bubbles for each minute meaning in these ideal circumstances $125,000,000$ bubbles will each discharge 0.0057 ergs onto the wafer surface. The total energy to the wafer surface is $712,500 \text{ ergs}$ or 0.071 Joules .

Bikerman (9) indicates that the force associated with a breaking bubble and associated void closure can be expressed:

$$Force = 4\pi r\gamma \text{ (dynes).}$$

Using the same parameters as above, the force is 1.88 dynes .

Menon (15), in discussing megasonics particle removal, indicates that a 300W megasonics transducer operating at full power (16) can produce an acceleration of $2.5 \times 10^8 \text{ cm/sec}^2$, and a dislodging force on a 1μ particle of $1.25 \times 10^{-4} \text{ dynes}$.

In the foam example, the corresponding acceleration can be estimated by dividing the force value by the mass of the fluid involved:

$$Mass = \pi r^2 \delta \rho$$

Delta, δ , is defined as the wall thickness, 0.001 cm , assumed, and ρ is the fluid density, 1.0 gm/cm^3 . This combination reduces to:

$$Acceleration = 4\gamma/r\delta\rho.$$

Substituting the appropriate values yields the acceleration of the water mass coming from the collapsing bubble, $0.66 \times 10^8 \text{ cm/sec}^2$, which is in reasonable agreement with the megasonic value.

The conclusion is: megasonics and foam bubbles can deliver approximately equivalent amounts of energy to the substrate wafer, therefore suggesting that foam only should be a cleaning medium for semiconductor wafers. Additionally, since the foam medium will be generated externally any heat accumulation problem in the cleaning vessel will be avoided.

Discussion

These proof-of-concept experiments were designed to demonstrate relative cleaning performance – cleaned vs. unprocessed and liquid cleaned vs. foam cleaned. The absolute cleaning performance varied depending on the cleaning fluid composition and the exposure. Evaluation of the results on the basis of absolute performance and other secondary effects is contrary to the experimental objectives.

The concept that photoresist residue can be removed without conventional remover chemicals is contrary to current thinking, although this goal is the objective of considerable effort. The idea that photoresist residue can be removed in a DI water medium, only by the action of bubbles arising from an aqueous foam medium, would be likely considered an unobtainable goal (17).

In order to support the “foam only” hypothesis, a wafer specimen [S] with generous residue remaining was subjected to treatment with a DI water solution containing 0.6 wt% DDBSA (Na+) actives and 0.18 wt% NCW601A actives. The treatment cycle was 10 minutes of chemical contact, followed by a one minute rinse, then followed by another 10 minutes chemical contact, and finally a 2 minute rinse and drying with nitrogen. In the liquid phase application, the wafer specimen was supported in a stirred beaker containing the fluid. In the foam application, nitrogen was added to the liquid phase generating a foam “head” in the upper portion of the vessel, and the wafer specimen was supported in the foam zone.

The SEM photographs exhibit unambiguous results. The unprocessed wafer is shown in Figure 1, the liquid phase treated wafer in Figure 2, and the foam treated wafer in Figure 3.

The conclusion is: the collapse of the bubbles, generated by the addition of nitrogen expansion gas to a reduced surface tension aqueous solution, cleaned the photoresist residue from the wafer surface. The same solution treating the same wafer substrate in the liquid phase showed essentially no cleaning.

Two wafer samples [S and T] were cleaned in both the liquid phase and the foam phase using three different EKC formulations, EKC 640, EKC 640D, and EKC BHX. The unprocessed wafer SEM photographs are Figure 1 [S] and Figure 4 [T].

Comparing Figure 5 (liquid) and Figure 6 (foam), each with EKC 640, it is clear that both were cleaned about equally well showing major improvement over the unprocessed wafer, Figure 4.

Wafer [S] was cleaned with EKC 640D in both the liquid phase and foam phase. Comparing Figure 7 and Figure 8 to the unprocessed [S] wafer, Figure 1, the conclusion is the same – both liquid and foam phases cleaned about equally and removed major amounts of residue material from the wafer structure.

Similarly, when wafer [S] was cleaned with EKC BHX the results were comparable to the liquid system – Figure 9 is the foam cleaned result while the unprocessed [S] wafer is Figure 1. The liquid system SEM photograph is not presented.

The conclusion is: a cleaning formulation delivered as foam to the surface of a semiconductor wafer will provide the wafer surface with a composition equivalent to a condensed phase liquid system,

yielding equivalent cleaning results.

Experimental

Two different proprietary wafers were used in the cleaning experiments. Each wafer surface was contaminated with photomask residue from the previous removal process. The wafers are designated [T] and [S] and their unprocessed initial condition is characterized in the SEM photographs – Figure 1 and Figure 4.

Three chemical cleaning compositions were used in both the liquid phase and the foam phase – EKC 640, EKC 640D, and EKC BHX002. These compositions are proprietary.

Two surfactants were used to make these compositions foamable. The NCW601A was obtained from Wako Chemical (Richmond, VA), and the DDBSA(Na+) was laboratory material obtained from Aldrich. These materials were readily available and no attempt was made to evaluate other surfactant materials. Since some the chemical cleaning compositions contained relatively low levels of water, the surfactant levels required for foaming were, by necessity, relatively high. No optimization efforts were made – when the substance foamed, the experimental conditions were defined as satisfied. The presence of sodium ion, normally considered a negative, was not considered important with respect to the objectives of these experiments.

The liquid phase cleaning experiments (beakers) involved suspending the wafer fragment, one sq. cm., in 100 cc. of the cleaning medium stirred magnetically at room temperature for the designated time period.

The corresponding foaming compositions were placed in a tall cylindrical vessel equipped with a gas dispersion tube for supplying nitrogen. Proper adjustment of the gas flow generated foam “head” above the liquid phase. The wafer fragment was suspended in this foam for the designated time period.

When the treatment process was completed the wafer fragments were rinsed with DI water for two minutes and dried with nitrogen gas.

Table I provides a summary of the cleaning compositions, the experimental conditions, and the Figures showing the SEM photographs.

Conclusions

The information obtained from these proof-of-concept experiments satisfy the objectives:

- (1) Liquid phase wafer cleaning compositions delivered to a semiconductor wafer substrate in a foam medium will deliver good cleaning performance.
- (2) Energy from collapsing foam bubbles will clean a semiconductor wafer substrate without the use of cleaning compositions.
- (3) Both theory and practice support the conclusion that megasonic cavitation and collapsing foam bubbles can deliver cleaning energy to a semiconductor wafer substrate.
- (4) These data suggest that DI water only cleaning technology may be an achievable goal.

References

- (1) For a comprehensive technical discussion about foam properties, see: Bikerman, J. J., “Foams,” Springer-Verlag, New York, NY, 1973, ISBN 0-387-06108-8.
- (2) For a more general discussion about foam characteristics, see: Perkowitz, Sidney, “Universal

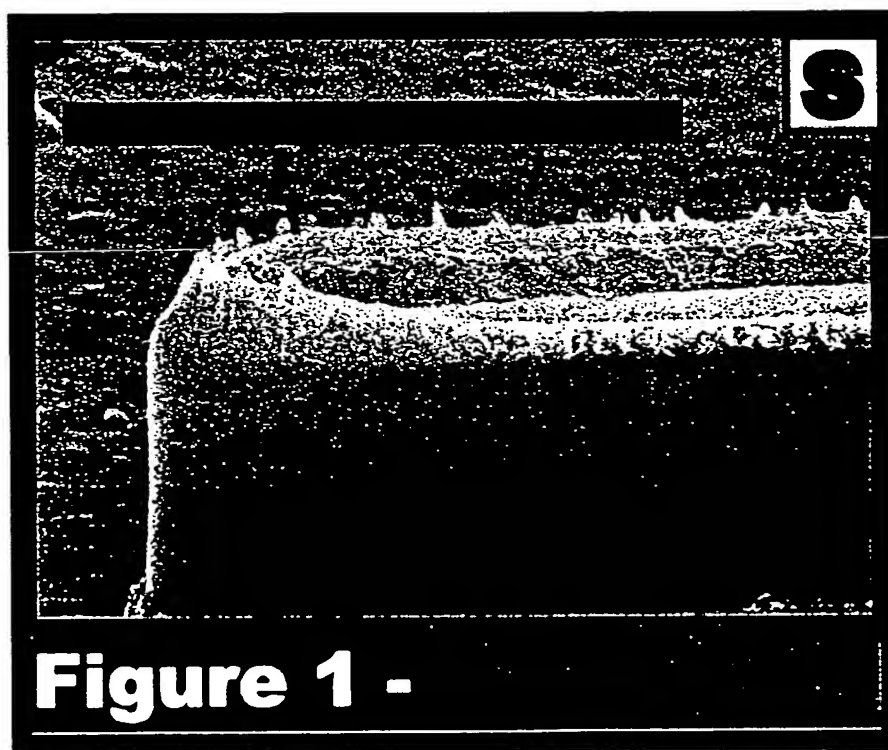
- Foam: From Cappuccino to the Cosmos," Walker & Company, New York, NY, 2000, ISBN 0-8027-1357-2.
- (3) Ogaya, K., "Washing Method for Semiconductor Device," Japanese Patent 63-239982-A2, October 5, 1988.
 - (4) Liu, B. Y. H. and Ahn, K. H., "System for Surface and Fluid Cleaning," U.S. Patent 4,817,652, April 4, 1989.
 - (5) Leenaars, A. F. M., "Method of Removing Undesired Particles from a Surface of a Substrate," U.S. Patent 4,781,764, November 1, 1988.
 - (6) Kittle, Paul A., "Particulate Removal Using a Foam Medium," A2C2, October, 2001. A more fully referenced version is also available on the Internet at: <http://www.aquafoam.com/particulate.html>. See also, Kittle, P. A., "Surface Treatment of Semiconductor Substrates," U.S. Patent 6,090,217, July 18, 2000.
 - (7) Reference (1), Chapter 3, page 65ff.
 - (8) See, for instance, Kern, W., Editor, "Handbook of Semiconductor Wafer Cleaning Technology – Science, Technology and Applications," Noyes Publications, Westwood, NJ, 1993, pages 141-142 and 421-424, ISBN 0-8155-1331-3.
 - (9) Reference (1), Chapter 1, page 11ff and Chapter 3, page 85ff.
 - (10) Dupre, A., "Theorie Mecanique de la Chaleur," Gauthier-Villars, Paris, 1869, page 350.
 - (11) Culick, F.E.C., J. Applied Physics, 31, 1128 (1960).
 - (12) Frankel, S. and Mysels, K.J., "The Bursting of Soap Films. II. Theoretical Considerations," J. Phys. Chem. 73, 3028 (1969).
 - (13) Rosen, M.J. and Solash, J., J. Am. Oil Chem. Soc., 46, 399 (1969).
 - (14) Reference (1), Chapter 7, page 189ff.
 - (15) Menon, V. B. and Donovan, R. P., "Reviewing Particle Control Issues Associated with Silicon Wafer Cleaning," Microcontamination, 8, 29-34, 66 (1990).
 - (16) Pre-Tech, Inc., Japan, Technical Bulletin, 1988.
 - (17) Hand, A., "Wafer Cleaning Confronts Increasing Demands," Semiconductor International, 24, 62-66 (2001).

Table I
Foam Wafer Cleaning
Cleaning Fluid Composition

Figure Number	Fluid Wafer	Fluid Medium	EKC Chemical	Surfactant A Name	Surfactant A Wt %	Surfactant B Name	Surfactant B Wt %	Treating Time*
1	S	Unprocessed						
2	S	Beaker		NCW601A	0.6	DDBSA(Na+)	0.6	10/1/10

3	S	Foam		NCW601A	0.6	DDBSA(Na+)	0.6	10/1/10
4	T	Unprocessed						
5	T	Beaker	640	NCW601A	3.0			20
6	T	Foam	640	NCW601A	3.0			20
7	S	Beaker	640D			DDBSA(Na+)	3.0	5/1/5
8	S	Foam	640D			DDBSA(Na+)	5.0	5/1/5
9	S	Foam	BHX002			DDBSA(Na+)	0.5	10/1/10

Note: 10/1/10, etc., denotes treatment time, rinse time, treatment time
 Final rinse, at least two minutes, followed by nitrogen gas drying
 All experiments at room temperature
 NCW601A, nonionic, water solution, 30% actives
 DDBSA(Na+), anionic, powder, 100% actives



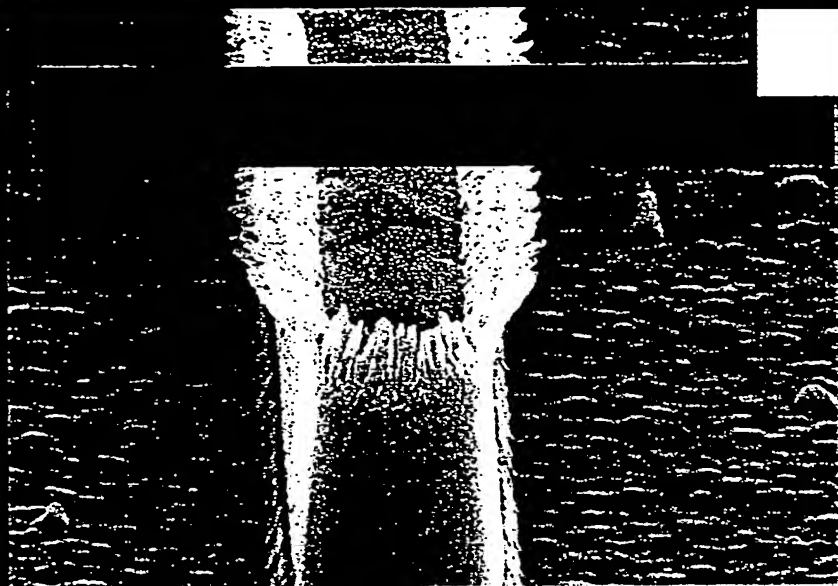


Figure 2 -

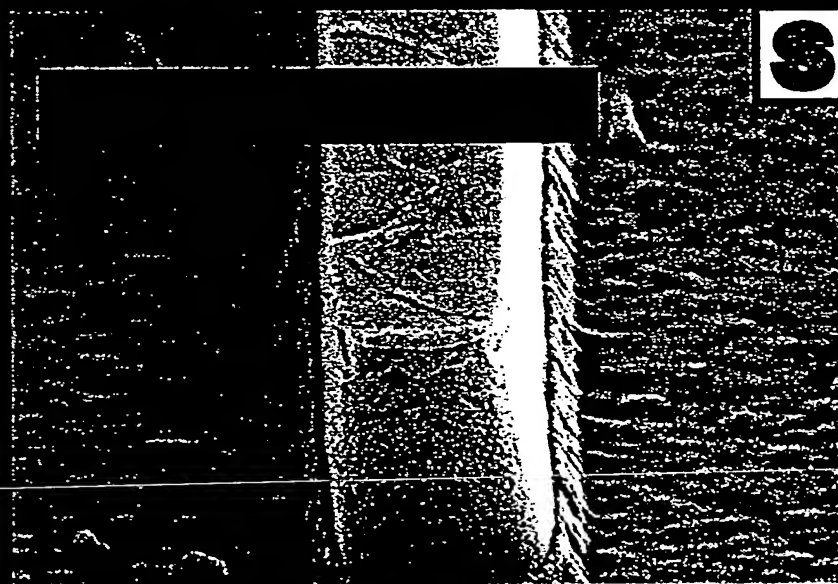


Figure 3 -

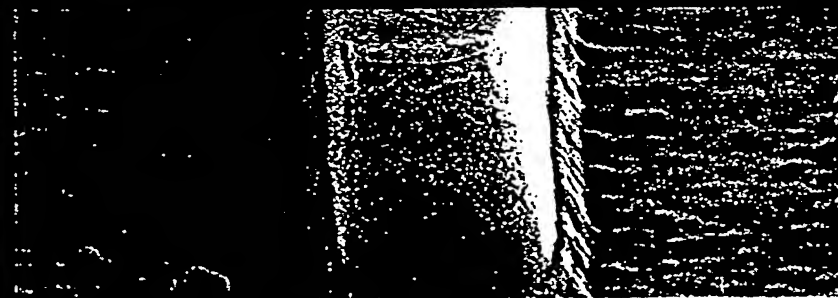


Figure 3 -



Figure 4 -

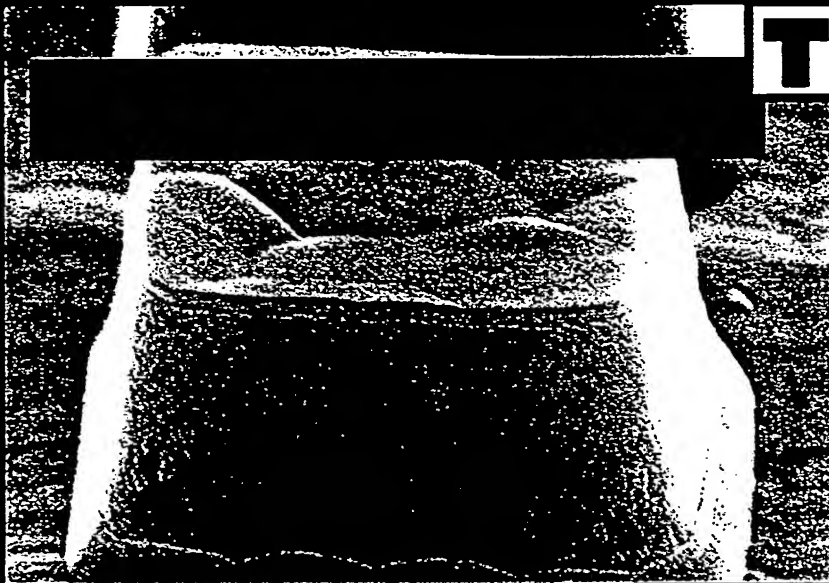


Figure 5 -

Figure 6 -

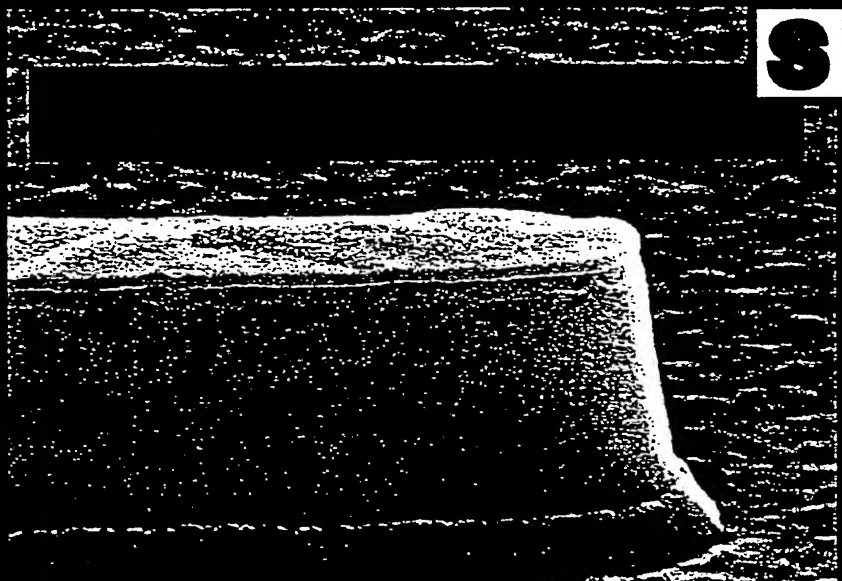


Figure 7 -

